

DIRECT ZnCl_2 HYDROCRACKING OF SUBBITUMINOUS COAL
- REGENERATION OF SPENT MELT

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INTRODUCTION

The use of molten metal halides of the Lewis acid type for the hydrocracking of coal and coal extract was extensively investigated by Consol Research in the period 1964-1967 under a research contract with the Office of Coal Research. A complete description of the work is available in reports to the OCR.^(1,2) Summary papers dealing with some of this work have also been presented.⁽³⁾

The above work concentrated most of its attention on the use of ZnCl_2 as the molten halide and on the use of bituminous coal extract as feed to the process. Hydrocracking of the extract⁽¹⁾ and regeneration by a fluidized-bed combustion technique of the spent catalyst melt⁽²⁾ from the process were both demonstrated in continuous bench-scale units.

A substantial program was also previously conducted in batch autoclaves on the direct hydrocracking of bituminous coal⁽¹⁾ with zinc chloride melts, but no work was done in either batch or continuous units on regeneration of spent melts from direct hydrocracking of coal.

Other workers have also examined direct hydrocracking of coal with molten metal halide catalysts. A large number of metal halide catalysts, for example, were examined for the direct hydrocracking of bituminous coal (Illinois No. 6) by Wald⁽⁴⁾ and co-workers and by Kivsky.⁽⁵⁾ However, little or no data are available either on the direct hydrocracking of lower rank coals with ZnCl_2 catalyst or on the regeneration of spent melts from such an operation. A large number of different coals ranging in rank from lignite to bituminous have more recently been tested in unpublished work at Consol Research. Almost all coals tested responded well to the ZnCl_2 hydrocracking technique.

The present paper presents batch autoclave data on the direct hydrocracking of a single subbituminous coal only from the Powder River basin of Southeastern Montana. Comparative data were also obtained with the Pittsburgh Seam bituminous coal that was used in the previous work.⁽¹⁾ Data on the regeneration of simulated spent melts from such an operation are also given in a continuous bench-scale, fluidized-bed combustion unit.

EXPERIMENTAL

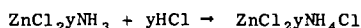
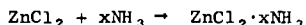
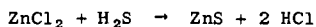
A. ZnCl_2 Hydrocracking - Batch Autoclave Work

All tests were made in a 316 stainless steel, 300 ml rocking autoclave. The equipment, the product workup, analytical and calculational procedures employed are all identical to those previously described.⁽¹⁾ A constant hydrogen partial pressure was used in each run by monitoring it with a palladium-silver alloy probe within the autoclave. The sensitivity of the probe response was increased as compared with prior work by heat treating at 1100°F for four hours before use. Subbituminous coal from the Colstrip Mine in Southeastern Montana was used in this work. Its analysis is given in Table I. The residence time at temperature was 60 minutes in all the runs reported here.

B. Regeneration by Fluid Bed Combustion

1. Preparation of Feedstock

During the hydrocracking process, the ZnCl_2 catalyst becomes contaminated with ZnS , $\text{ZnCl}_2 \cdot \text{NH}_3$ and $\text{ZnCl}_2 \cdot \text{NH}_4\text{Cl}$ that are formed by the ZnCl_2 catalyst partially reacting with the sulfur and nitrogen liberated from the feed in the hydrocracking step:



The proportions of $\text{ZnCl}_2 \cdot x\text{NH}_3$ and $\text{ZnCl}_2 y\text{NH}_4\text{Cl}$ depend on the ratio of nitrogen and sulfur in the feed. In addition to these inorganic compounds, the catalyst leaving the hydrocracker also contains residual carbon that cannot be distilled out of the melt. In the case of direct coal hydrocracking, the catalyst also contains the coal ash.

The melt used in this work was prepared from the residue of hydrogen-donor extraction of Colstrip coal with tetralin solvent in such a way as to simulate the composition of an actual spent melt. The extraction was conducted in the continuous bench-scale unit previously described⁽²⁾ at 775°F and 50 minutes residence time. The residue used was the solvent-free underflow from continuous settling⁽⁶⁾ of the extractor effluent. The residue was then precarbonized to 1250°F in a muffle furnace. The melts were blended to simulate the composition of a spent melt from the direct hydrocracking of the Colstrip coal by blending together in a melt pot ZnCl_2 , ZnS , NH_4Cl , NH_3 and the carbonized residue in appropriate proportions. Analysis of the feed melt used in this work is given in Table II.

2. Equipment and Procedure

Figure 1 is a diagram of the continuous, 2-7/8" ID fluidized bed combustion unit that was used. The melt is fed via syringe feeders and is dropped from a remote drip tip into a batch bed of fluidized solids that is fluidized by feed air that enters at the apex of the reactor cone. The carbon, nitrogen and sulfur are burned out in the fluidized bed and the ZnCl_2 is vaporized. The gas, ZnCl_2 vapor and elutriated solids leaving the reactor pass through the cyclone where the solids are collected. The cyclone underflow solids derive solely from the melt since the sizing of the bed solids is such that there is essentially no elutriation of this material. The solids collected at the cyclone then include coal ash, zinc oxide formed by hydrolysis of zinc chloride, and any unburned carbon or zinc sulfide. The gas then passes to the condenser where ZnCl_2 is condensed out, then to the electrostatic precipitator to remove ZnCl_2 fog and then to sampling and metering.

The analytical methods and calculational procedures are substantially the same as those previously described.

RESULTS AND DISCUSSION

Hydrocracking

A series of experiments were carried out at a relatively low temperature and hydrogen partial pressure of 358°C and 103 atms, respectively. Comparison runs were carried out with the Pittsburgh Seam coal from the Ireland Mine used in the previous work. Selected results are given in Table II.

The previous work with bituminous coal at these mild conditions was carried out without a hydrocarbon vehicle. These data are reproduced in the last column of Table II.

Attempts to run with the subbituminous coal at the above mild conditions without a vehicle were not successful due to a formation of a high viscosity mix which made temperature control very poor and yielded erratic results.

Methylnaphthalene was then used as a vehicle, but even in this case very poor results were obtained, i.e., conversion to MEK solubles and distillate products was very low. Results of this run are not reported since they are obscured by extensive cracking of the solvent.

The use of tetralin as a hydrogen-donor solvent, however, gave a very good conversion to MEK soluble products as shown in Table II. In this case, also some cracking of the solvent occurred, but the hydrogen consumption and gaseous products are calculated neglecting any contribution made to these quantities by hydrogenation and cracking of the tetralin.

The addition of a hydrogen-donor solvent to the subbituminous coal at these mild conditions, appear to be required to assist in melting of the coal to permit access of the molten halide catalyst.

The highly fluid Pittsburgh Seam coal, on the other hand, does not require addition of a vehicle as the data of Table II show. As a matter of fact, superior results were obtained in the absence of a vehicle although the difference may be due to the fact that in one case a cleaned coal was used, i.e., the poorer results with the vehicle may reflect some adverse effect of the mineral matter on the hydrocracking process. Also, a somewhat lower catalyst/coal feed ratio was used in the run without a vehicle.

Operation at these mild conditions are of interest where the objective is to produce low-sulfur fuel oil in major amounts as a co-product with gasoline. Previous work has shown that 65-80% of the MEK solubles may be recovered from the spent melt by extraction with a fraction of the distillate oil product. The data of Table IV, interestingly enough, show that the MEK soluble oil contains less than 0.2 wt % sulfur even when the high sulfur Pittsburgh Seam coal is used as feedstock.

The total liquid yield, i.e., C_4 through MEK soluble hydrocarbons at these mild conditions is almost as high with the subbituminous coal, i.e., 74.4 wt % of the MAF coal as with the bituminous coal, i.e., 75.5 and 76.7 wt % of the MAF coal with and without the use of a vehicle, respectively. The hydrogen consumption, on the other hand, is significantly lower for the subbituminous case. This is primarily because of the lower gas and distillate yields. The yield of heavy fuel oil, i.e., MEK soluble oil is significantly higher in the case of the subbituminous coal.

If the temperature and pressure is increased, then a vehicle is no longer necessary even in the case of the subbituminous coal. A series of experiments were carried out without a vehicle using a hydrogen partial pressure of 205 atm and at temperatures ranging from 370 to 427°C. The $ZnCl_2/MF$ feed ratio and the reaction time were held constant at 2.5/1 and 60 minutes, respectively, in these runs.

The above series of runs showed that two optimum temperatures existed. The first at about 385°C gave a maximum conversion to MEK soluble and lighter products of about 95%. The second at about 410°C gave a maximum conversion to gasoline expressed as $C_4 \times 200^\circ C$ distillate of about 60 wt % of the MAF coal.

More detailed results of two runs, each near the above two optimum temperatures are given in Table III. Comparison is also given with results obtained with Ireland Mine coal at the lower of the above two temperatures.

It is noted that the conversions and hydrogen consumptions are very nearly the same for both coals. The yield of hydrocarbon distillates and particularly gasoline is about 20% higher for the bituminous coal case. The hydrogen consumption per unit of liquid distillate hydrocarbons produced is about 15% higher for the subbituminous coal case. The above differences are to be anticipated and are a result of the higher hydrogen and lower oxygen contents as noted in Table I of the bituminous coal.

The sulfur content of the MEK soluble oil is again as noted in Table IV very low.

Regeneration via Fluid Bed Combustion

Table V gives the conditions of runs presented here - essentially atmospheric pressure, superficial residence time of one second, excess air, i.e., 115% of stoichiometric, silica bed solids. Temperatures of 1800 and 1900°F were investigated. No operability problems such as ash agglomeration or defluidization of the bed were encountered at these conditions.

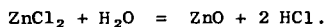
Table VI gives the distribution of carbon, sulfur and nitrogen in the products for runs at 1800 and 1900°F. One-hundred fifteen percent of stoichiometric air was used in both runs. The feed gas was pure air. It is apparent that the carbon, nitrogen and sulfur impurities almost completely burned out, i.e., 89% or more burn-out was achieved. The effluent melt contains less than 3% of the carbon and sulfur in the feed melt and 11% or less of the nitrogen.

Table VII shows the distribution of total coal ash as well as the coal ash components, silica and alumina, in the products in two runs at 1800°F. In Run 3, the feed gas was 100% air while in Run 11, the feed gas was 94.5% air and 5.5% anhydrous HCl. The HCl was added to prevent hydrolysis of the $ZnCl_2$. This will be discussed further later. Eighty-nine percent or more of the total coal ash and silica and alumina were removed from the melt in the regeneration process. The ashes were either trapped in the bed or collected at the cyclone.

Table VIII shows the distribution of the ash components, iron, calcium, and magnesium in the products of the same two runs as in Table VII. Again, it is apparent that the large majority of these ash components were removed from the melt and that they were either trapped in the combustor bed solids or collected at the cyclone.

The distribution of sodium and potassium is not given in the tables. Essentially all of the sodium and potassium in the feed appears in the effluent melt. This is likely due to the potassium and sodium being converted into the chlorides which are sufficiently volatile to be vaporized along with the $ZnCl_2$. This chlorine is considered to be irrecoverable. Hence, this method of regeneration is chiefly useful with coals that have relatively low alkali concentrations.

Table IX shows the distribution of zinc and chlorine among the products in Runs 3 and 11. The feed gas in Run 3 was pure air. In this run, about 10% of the feed zinc was found in the bed solids and cyclone solids as ZnO while 90% is in the melt as $ZnCl_2$. The large amount of ZnO is formed by hydrolysis of $ZnCl_2$ in the combustor,



Because of the hydrolysis, a large amount of the chlorine in the feed melt is found in the gas as HCl. For the process to be economically feasible, ZnCl_2 would have to be reformed from the ZnO and HCl products.

To preclude such a step, the HCl can be recycled with the feed air to prevent hydrolysis. Run 11 was made to test this concept where the feed gas contained 5.5% anhydrous HCl. The chlorine in the feed HCl amounted to 14.8% of the chlorine in the ZnCl_2 feed. It is apparent that hydrolysis was almost completely suppressed and that the Zn in the feed melt was almost totally converted to and recovered as ZnCl_2 .

Before starting this work, it was feared that considerable chlorine would be lost as CaCl_2 by interaction of the calcium in the coal ash with the ZnCl_2 , but it appears that essentially no chlorine is lost in this manner. It will be noted in both Runs 3 and 11, that the bed solids contain substantially no chlorine whereas they contained a large percentage of the calcium that was fed. Since CaCl_2 is molten but nonvolatile at combustion temperature, it would be expected that any calcium chloride would be retained in the bed solids. Since none was, it is concluded that no calcium chloride was formed. (It also appears that no magnesium chloride was formed.)

Table X shows some pertinent reactions in the regeneration system. We determined the equilibrium constant for reaction (3) and obtained P_{ZnCl_2} of 57 torr whereas P_{ZnCl_2} in the combustor was about 120 torr. Hence, it might be expected that some CaCl_2 would be formed. It is believed that the reason we didn't get CaCl_2 is because of reactions such as (4) and (5) whose equilibria are probably far to the right. Kuxmann and Oder⁽⁷⁾ have reported recovering zinc as pure ZnCl_2 vapor from impure ores by reaction (4) carried out at about 1650°F.

It appears that some FeCl_2 is formed but not in the amount that would be expected if equilibrium had been established in reaction (2). Reactions analogous to (4) and (5) with FeCl_2 substituted for CaCl_2 may be the reason for this. In any case, the equilibrium constant indicates that the amount of FeCl_2 that can be formed is limited to 1 mol per 9 mols of ZnCl_2 . We have unpublished data that indicates that FeCl_2 does not affect catalyst activity.

We believe, based on the results just presented as well as other results, that fluid bed combustion provides a workable process for regenerating ZnCl_2 from direct hydrogenation of western subbituminous coals. Other work not presented here indicates that the process can also be successfully applied to melts from direct hydrogenation of eastern bituminous coals also. The process is, however, restricted to coals having relatively low sodium and potassium contents so that economically prohibitive amounts of chlorine are not lost to these alkali metals. Lignites are the major type of coal that would be ruled out by the above restriction.

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TABLE I

Analysis of FeedstocksA. Proximate & Ultimate

	<u>Coals</u>			Regeneration Feedstock "Spent" Melt
	<u>Colstrip</u>	<u>Cleaned Ireland Mine</u>	<u>Ireland Mine</u>	
<u>Wt % MF Basis</u>				
Volatile Matter	37.3	43.4	42.5	--
Non Oxidized Ash	9.7	6.4	9.1	1.78
Organic (Hydrogen)	4.4	5.3	5.3	0.11
Carbon	68.0	76.5	74.5	5.03
Organic (Nitrogen)	1.1	1.6	1.1	0.09
Oxygen (by Diff)	16.1	8.3	7.7	0.24
Organic Sulfur	0.5	1.9	2.3	0.04
Pyritic Sulfur	0.2	0.9	1.7	--
Sulfate Sulfur	0.04	0.0	0.08	--
ZnCl ₂	--	--	--	85.34
ZnS	--	--	--	2.92
NH ₄ Cl	--	--	--	3.20
NH ₃	--	--	--	1.25

B. Ash Composition (Oxidized & SO₃ Free Basis)

P ₂ O ₅	--	--	--	0.15
SiO ₂	43.9	41.0	43.5	42.2
Al ₂ O ₃	26.0	20.4	24.6	25.3
Na ₂ O	0.25	0.6	0.5	0.47
K ₂ O	0.15	1.5	1.6	0.21
CaO	17.3	2.8	1.7	18.7
MgO	6.7	0.7	0.7	7.1
Fe ₂ O ₃	4.7	29.6	22.8	4.6
TiO ₂	1.0	1.1	1.0	1.4

TABLE II

Hydrocracking at "Mild" ConditionsA. Constant Conditions for All Runs

Temperature	358°C
Time at Temperature	60 minutes
Total Time Above 315°C	70 minutes (approx.)
H ₂ Partial Pressure During Hydrocracking	103 atm. abs.
Coal Particle Size	-100 mesh

B. Variable Conditions and Yields

Coal	<u>Colstrip</u>	<u>Ireland Mine</u>	<u>Cleaned Ireland Mine</u>
<u>Gms Feed/gm MF Coal</u>			
ZnCl ₂	2.5	2.5	2.0
Solvent	0.5	0.5	0.0
Solvent Used	Tetralin	Tetralin	None
<u>Yields, Wt % MAF Coal</u>			
(C ₁ -C ₃) Hydrocarbons	1.7	5.1	5.2
(CO + CO ₂) Gas	5.5	0.8	0.1
(H ₂ O)	12.3	7.2	8.7
C ₄ x 400°C Distillate	27.5	43.8	56.4
+400°C MEK Soluble	46.9	31.3	20.3
+400°C MEK Insoluble	10.5	16.5	12.8
N ₂ O, S + H to Catalyst	<u>1.5</u>	<u>2.8</u>	<u>3.0</u>
Total	105.9	107.5	106.5
H ₂ Consumed, Wt % MAF Coal	5.9	7.5	6.5
<u>Wt. % Conversion MAF Coal</u>			
To - 400°C Products	42.6	52.2	66.9
To - 400°C + MEK Solubles	89.5	83.5	87.2

TABLE III
Hydrocracking at "Severe" Conditions

A. Constant Conditions for All Runs

Time at Temperature	60 minutes
Total Time Above 315°C	70 minutes
ZnCl ₂ /MF Coal Feed Ratio	2.5
H ₂ Partial Pressure	205 atm. abs.
Coal Particle Size	-100 mesh

B. Yields and Conversions, Wt. % MAF Coal

Coal	<u>Colstrip</u>	<u>Colstrip</u>	<u>Ireland Mine</u>
Temperature, °C	385	413	385
CH ₄	0.6	1.3	0.4
C ₂ H ₆ + C ₃ H ₈	4.8	8.6	8.3
C ₄ x 200°C Distillate	55.6	59.0	66.4
200 x 400°C Distillate	3.1	1.2	2.2
+400°C MEK Soluble	17.1	9.2	13.9
+400°C MEK Insoluble	5.2	8.7	6.0
CO + CO ₂ + H ₂ O	19.9	19.3	8.6
N, O, S + H to Catalyst	<u>2.4</u>	<u>2.2</u>	<u>3.3</u>
Total	108.7	109.5	109.1
H ₂ Consumed, Wt. % MAF Coal	8.7	9.5	9.1
<u>Wt. % Conversion MAF Coal</u>			
To - 400°C Products	77.7	82.1	80.1
To - 400°C + MEK Solubles	94.8	91.3	94.0
Total - 400°C Hydrocarbons	64.1	70.1	77.3
<u>Total - 400°C Hydrocarbons</u>			
H ₂ Consumed	7.4	7.4	8.5

TABLE IV
Sulfur Content of +400°C MEK Soluble Oil

Coal	<u>Colstrip</u>		<u>Ireland Mine</u>	
Temperature, °C	358	385	358	385
H ₂ Partial Pressure, atm	103	205	103	205
% Sulfur in MEK Solubles	0.17	0.04	0.17	0.18

TABLE VGENERAL CONDITIONS

PRESSURE , PSIG	2.0
SUPERFICIAL AIR VELOCITY, FPS	1.0
SUPERFICIAL RESIDENCE TIME, SEC.	1.0
MELT FEED RATE, LB/HR.-FT. ²	73
% OF STOICHIOMETRIC AIR	115
FLUIDIZED BED DEPTH, INCHES	12
TYPE OF BED SOLIDS	28 x 48M SILICA

TABLE VI

DISTRIBUTION OF C, S AND N IN THE PRODUCTS

RUN NUMBER	3	4
TEMP. , °F	1800	1900
% of STOICH. AIR	115	115
DISTRIBUTION of C, %		
BURNED to CO ₂ (+ LOSS)	92.7	92.9
BURNED to CO	5.9	4.2
IN CYCLONE SOLIDS	0.4	0.5
IN MELT	1.0	2.4
DISTRIBUTION of S, %		
BURNED to SO ₂ (+ LOSS)	91.3	96.4
IN BED	1.8	0.4
IN CYCLONE SOLIDS	3.8	1.4
IN MELT	3.1	1.8
DISTRIBUTION of N, %		
NH ₃ BURNED to N ₂ + H ₂ O (+LOSS)	89.3	100.0
N IN MELT	10.7	0.0

TABLE VII

DISTRIBUTION OF TOTAL COAL ASH, Si, Al, AMONG THE PRODUCTS

RUN NUMBER	3	11
TEMP., °F	1800	1800
<u>FEED GAS COMP., MOL %</u>		
AIR	100	94.5
ANHYDROUS HCl	-	5.5
<u>DIST. OF TOTAL ASH, %</u>		
BED SOLIDS (+ LOSS)	19	34
CYCLONE SOLIDS	70	59
MELT	11	7
<u>DIST. OF Si, %</u>		
BED SOLIDS (+ LOSS)	29	28
CYCLONE SOLIDS	67	68
MELT	4	4
<u>DIST. OF Al, %</u>		
BED SOLIDS (+ LOSS)	94	31
CYCLONE SOLIDS	}	64
MELT	6	5

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TABLE VIII

DISTRIBUTION OF Fe , Ca , Mg AMONG THE PRODUCTS

RUN NUMBER	3	11
TEMP. , °F	1800	1800
<u>FEED GAS COMP. , MOL %</u>		
AIR	100	94.5
ANHYDROUS HCl	-	5.5
<u>DIST. OF Fe , %</u>		
BED SOLIDS (+ LOSS)	73 }	0
CYCLONE SOLIDS		61
MELT	27	39
<u>DIST. OF Ca , %</u>		
BED SOLIDS (+LOSS)	29	53
CYCLONE SOLIDS	48	42
MELT	23	5
<u>DIST. OF Mg , %</u>		
BED SOLIDS (+LOSS)	44	57
CYCLONE SOLIDS	43	41
MELT	13	2

TABLE IX

DISTRIBUTION OF ZINC AND CHLORINE IN THE PRODUCTS

<u>RUN NUMBER</u>	<u>3</u>	<u>11</u>
TEMP., °F	1800	1800
<u>FEED GAS COMP., MOL %</u>		
AIR	100	94.5
ANHYDROUS HCl	-	5.5
<u>Cl DIST., % OF Cl IN FEED MELT</u>		
BED SOLIDS	.02	.01
CYCLONE SOLIDS	.44	.30
GAS	9.10	14.50
MELT (+LOSS)	<u>90.40</u>	<u>100.00</u>
TOTAL	100.00	114.80
<u>Zn DIST., % OF Zn IN FEED MELT</u>		
BED SOLIDS	5.5	.40
CYCLONE SOLIDS	4.4	.74
MELT (+LOSS)	90.1	98.90

TABLE X

SOME PERTINENT REACTIONS

K at 1800°

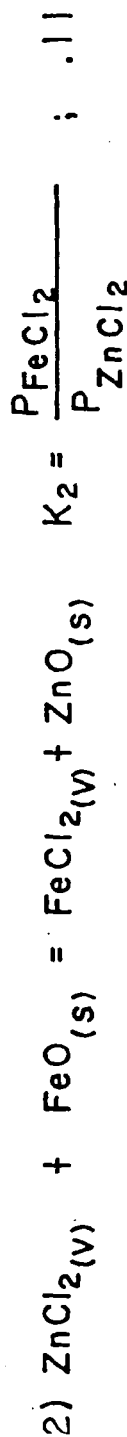


FIGURE 1

FLUIDIZED COMBUSTION UNIT

